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Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Sergei Porokhin

PhD Program: Materials Science and Engineering

Title of Thesis: Perovskite mixed oxides as catalysts of oxygen evolution reaction

Supervisor: Professor Artem Abakumov

Co-supervisor: Assistant Professor Victoria Nikitina

Name of the Reviewer: Nurxat Nuraje

I confirm the absence of any conflict of interest (Alternatively, Reviewer can formulate a possible conflict)	**Date: 11-09-2022**

The purpose of this report is to obtain an independent review from the members of PhD defense Jury before the thesis defense. The members of PhD defense Jury are asked to submit signed copy of the report at least 30 days prior the thesis defense. The Reviewers are asked to bring a copy of the completed report to the thesis defense and to discuss the contents of each report with each other before the thesis defense.

If the reviewers have any queries about the thesis which they wish to raise in advance, please contact the Chair of the Jury.

Reviewer's Report

Reviewers report should contain the following items:

- Brief evaluation of the thesis quality and overall structure of the dissertation.
- The relevance of the topic of dissertation work to its actual content
- The relevance of the methods used in the dissertation
- The scientific significance of the results obtained and their compliance with the international level and current state of the art
- The relevance of the obtained results to applications (if applicable)
- The quality of publications

The summary of issues to be addressed before/during the thesis defense

Review Report

on the PhD thesis by Sergei V. Porokhin entitled
"Perovskite Mixed Oxides as Catalysts of Oxygen Evolution Reaction"

Hydrogen is considered as a potential alternative to replace the current carbon-based energy since it has high energy density as an energy carrier and the by-product is water, which is environmentally benign, while the fuel cell generates the electricity using hydrogen and oxygen. Although the current technology of hydrogen production via steam reforming is relatively cheaper, it creates greenhouse gas such as CO_2. Water splitting to produce hydrogen and oxygen is a more attractive option due to it being ecofriendly. Among the different types of water splitting, water electrolysis is a promising direction to produce hydrogen and oxygen without emission of hazard and greenhouse gases. In water electrolysis, the oxygen evolution reaction including four electron transfer process is a critical step to improve overall water splitting efficiency. At present, development of an efficient OER electrocatalyst is highly desirable. In recent decades, pervoskite oxides have been drawn great attraction due to their promising catalytic activity, stability, and cost-effectiveness. Thus, in this thesis, NiFe-based perovskite catalyst is selected to further study OER mechanism to design highly-efficient, cost-effective and stable electrocatalysts.

The PhD thesis focused on the electrocatalytic properties of the three different types of catalysts: LFN ($LaFe_{0.25}Ni_{0.75}O_3$; $LaFe_{0.7}Ni_{0.3}O_3$), LCFN5 ($La_{0.5}Ca_{0.5}Fe_{0.7}Ni_{0.3}O_{3-\delta}$; $La_{0.6}Ca_{0.4}Fe_{0.7}Ni_{0.3}O_{2.9}$), and LCFN3 ($La_{0.7}Ca_{0.3}Fe_{0.7}Ni_{0.3}O_{3-\delta}$) and their oxygen evolution mechanism with changing active centers. Furthermore, three different types of catalysts were synthesized by a modified ultrasonic spray pyrolysis technique and their crystal structure and composition were determined by relevant characterization instruments including powder X-ray diffraction, electron diffraction, aberration-corrected scanning transmission electron microscopy, energy-dispersive X-ray mapping, ^{57}Fe Mössbauer spectroscopy, iodometric titration and X-ray photoelectron spectroscopy. It was found that the $La_{0.6}Ca_{0.4}Fe_{0.7}Ni_{0.3}O_{2.9}$ perovskite demonstrates a superior specific and mass activities. The enhanced activity of $La_{0.6}Ca_{0.4}Fe_{0.7}Ni_{0.3}O_{2.9}$ relative to undoped $LaFe_{0.7}Ni_{0.3}O_3$ was explained via DFT-simulation. The Ca doping increases Ni and Fe oxidation states, and caused faster leaching of A-site cations and restructuring of the surface layers of perovskite into Ni-Fe (oxy) hydroxides, which strongly interact with Fe ions in the electrolyte. As a result, the electrocatalytic activity of the perovskite materials is greatly enhanced.

The thesis also evaluated the effect of the most common impurity in alkaline electrolytes on the stability and activity of perovskite catalyst via OER experiments with the deliberate addition of Fe ions to the electrolyte. Transmission electron microscopy study confirmed the restructuring of the perovskite surface layer into $Ni_{0.5}Fe_{0.5}O_x(OH)_{2-x}$ via interaction of Fe ions in electrolyte with the perovskite surface.

The reliability of the results submitted for defense is not in doubt and is confirmed by published works in peer-reviewed high impact journals including *ACS Catalysis* (IF2021: 13.7) and *Materials* (IF2021: 3.748) included in the Scopus database and Web of Science. The main scientific results were discussed at international conferences.

The content of the thesis and the list of publications of the author on the research topic proved that the PhD thesis by Sergei Porokhin is a complete scientific research work and meets all the requirements for PhD theses. As the member of the jury, I think the candidate deserves to be awarded the degree of Doctor of Philosophy (PhD).

Provisional Recommendation

☒ *I recommend that the candidate should defend the thesis by means of a formal thesis defense*
☐ *I recommend that the candidate should defend the thesis by means of a formal thesis defense only after appropriate changes would be introduced in candidate's thesis according to the recommendations of the present report*
☐ *The thesis is not acceptable and I recommend that the candidate be exempt from the formal thesis defense*